

PHOTOCHROMIC MATERIAL

Cross reference to related application

[0001] This is a continuation application of
5 PCT/JP02/01946 filed on March 4, 2002.

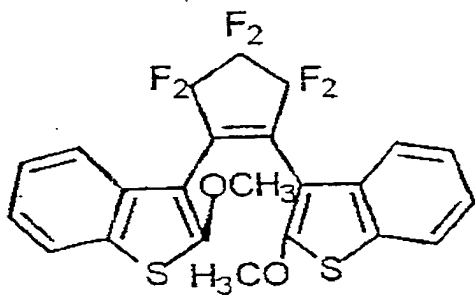
FIELD OF THE INVENTION

[0002] The present invention relates to a photochromic
material comprising a compound belonging to the
10 diheteroarylethene class.

BACKGROUND OF THE INVENTION

[0003] Photochromic material includes molecules or
molecule aggregates which can reversibly take the forms of
15 two isomers having different states by photoisomerization.
The photochromic material can be utilized as photonics
materials such as optical memory media and optical display
materials, because the photochromic material can change not
only its color but also its various other physical properties—
20 such as refractive index, dielectric constant, and
oxidation/reduction potential under irradiation of light.

[0004] Japanese Unexamined Patent Publication No.
H3-261782 discloses a photochromic material belonging to the
diheteroarylethane class, having methoxy groups at two
25 reactive positions participating in ring closing/ring
opening reactions, as expressed by the following formula:

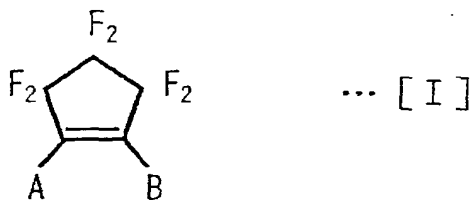


[0005] The record or image of the optical memory medium or optical display material of the photochromic material may disappear under ambient light such as a room light. When the quantum yield of ring opening reaction (hereinafter, referred to as "ring opening quantum yield") of a compound, belonging to the diarylethene class, in the closed-ring form is in the order of 10^{-2} , the record or image will disappear almost completely in several hours under fluorescent room light.

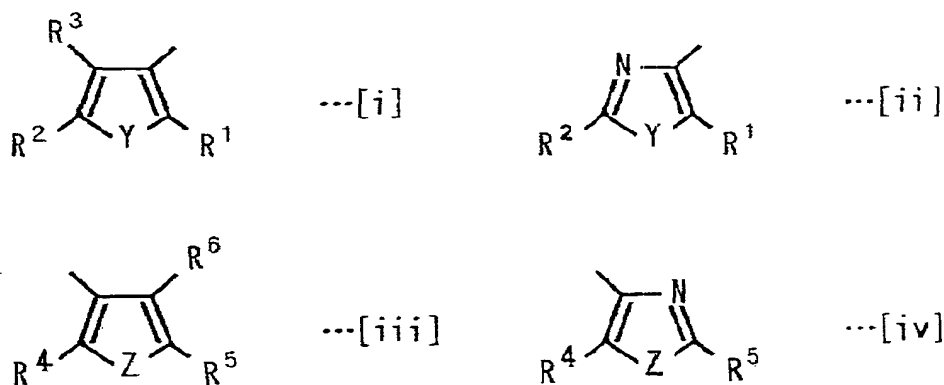
10 [0006] The aforementioned compound belonging to the diheteroarylethene class disclosed in Japanese Unexamined Patent Publication No. H3-261782 has a ring opening quantum yield of 3.3×10^{-2} , which is larger than 10^{-2} .

15 DISCLOSURE OF THE INVENTION

[0007] A photochromic material of the present invention comprises a compound, belonging to the diheteroarylethene class, represented by the following general formula [I]:



[0008] In the general formula [I], A represents substituents [i] or [ii] shown below, and B represents substituents [iii] or [iv] shown below.



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[0009] In the substituents [i] and [ii], R¹ represents an alkoxy group, and R² represents -Q-Ar. Q represents a direct bond or an arbitrary divalent group, and Ar represents an aromatic hydrocarbon ring or an aromatic heterocycle, which are optionally substituted. R³ represents a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a fluoroalkyl group, a cyano group, or an aryl group which is optionally substituted, and Y represents -O- or -S-.

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[0010] In the substituents [iii] and [iv], R⁴ represents

an alkoxy group, and R^5 represents $-Q-Ar$. Q represents a direct bond or an arbitrary divalent group, and Ar represents an aromatic hydrocarbon ring or an aromatic heterocycle, which are optionally substituted. R^6 represents a hydrogen atom,
5 an alkyl group, an alkoxy group, a halogen atom, a fluoroalkyl group, a cyano group, or an aryl group which is optionally substituted, and Z represents $-O-$ or $-S-$.

[0011] The photochromic material of the present invention has a ring opening quantum yield of 10^{-3} or lower.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] Hereinafter, the present invention will be described in detail.

[0013] A photochromic material of the present invention
15 comprises a compound, belonging to the diheteroarylethene class, represented by the abovementioned general formula [I].

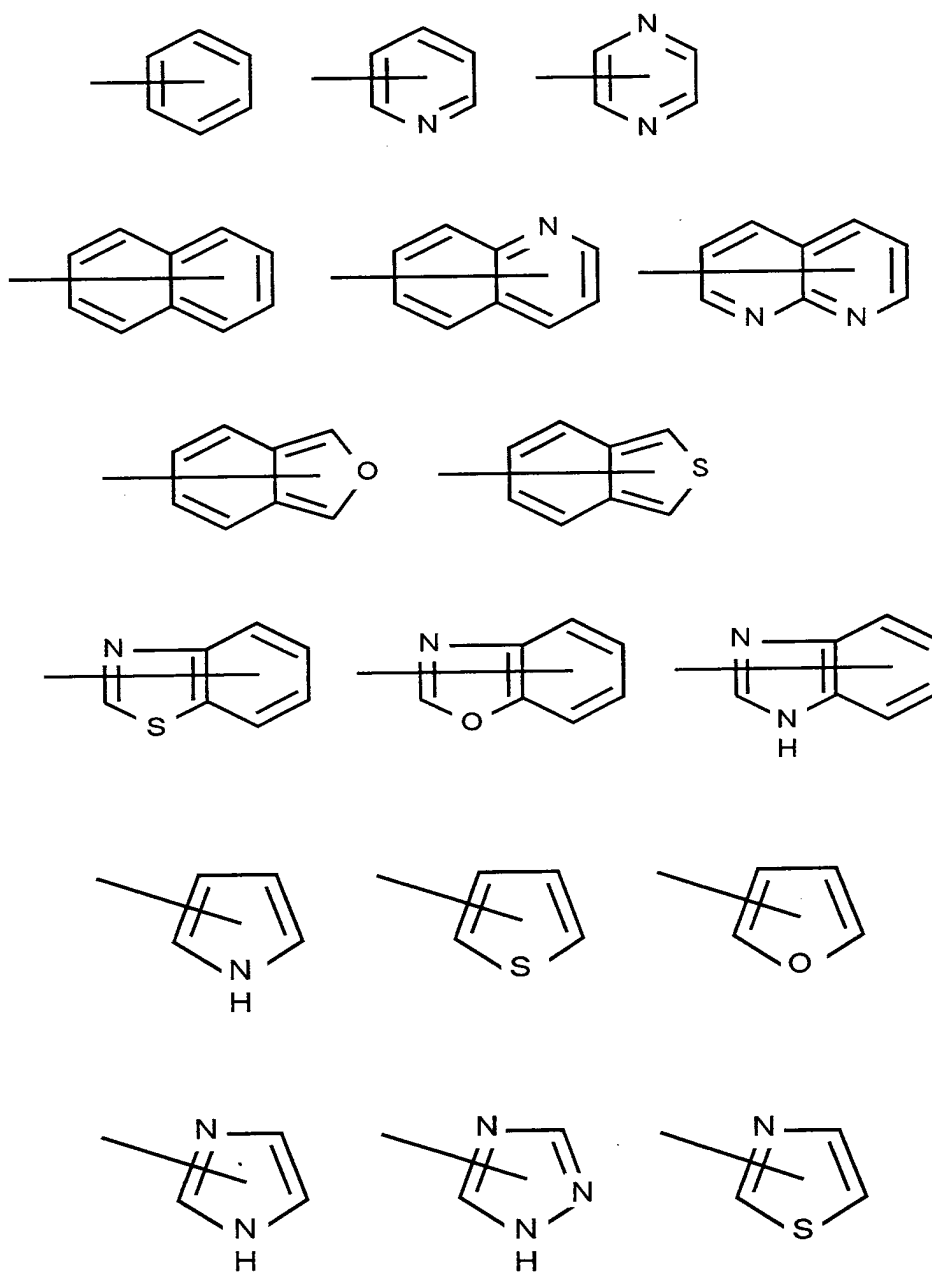
[0014] In the substituents [i]-[iv] of the general formula [I], R^1 and R^4 each represent independently alkoxy group with 1-3 carbon atoms such as methoxy group and ethoxy group,
20 preferably a methoxy group or an ethoxy group, more preferably a methoxy group.

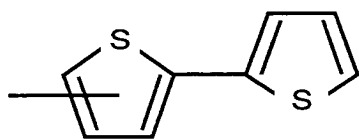
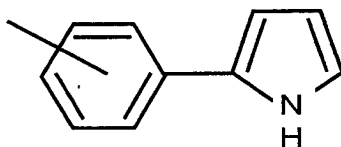
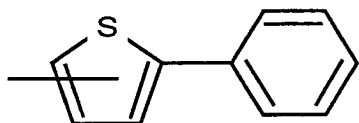
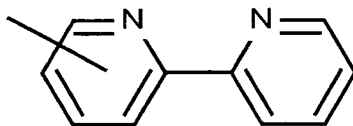
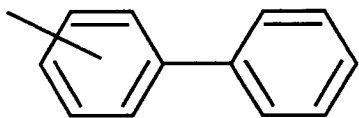
[0015] R^2 and R^5 each represent independently $-Q-Ar$. Q represents a direct bond or an arbitrary divalent group, and Ar represents an aromatic hydrocarbon ring or an aromatic
25 heterocycle, which are optionally substituted. In preferable structures, a conjugated system extends from both heteroaryl rings of the diarylethene structure to substituents R^2 and R^5 . In the general formula [I], Q preferably comprises a direct

bond, $-(\text{-CH=CH-})_n-$ (i.e. a polyethylene group) (wherein $n = 1-5$), or $-(\text{-C}\equiv\text{C-})_n-$ (i.e. a polyacetylene group) (wherein $n = 1-5$), and Ar preferably comprises a group consisting of 5- or 6-member ring or a group consisting of two or three 5- or 6-member rings bonded directly or condensed, each of the groups being optionally substituted. When Ar has a substituent, the substituent includes a linear or branched alkyl group with 1-10 carbon atoms such as methyl group, ethyl group, butyl group, and hexyl group; a linear or branched alkoxy group with 1-10 carbon atoms such as methoxy group, ethoxy group, butoxy group, and hexyloxy group; a halogen atom such as fluorine atom and chlorine atom; and linear or branched fluoroalkyl group with 1-6 carbon atoms such as trifluoromethyl group, pentafluoroethyl group, 2-fluoroethyl group, 2,2-difluoroethyl group, perfluoro-n-hexyl group, and 2-(perfluorobutyl)ethyl group.

[0016] In a diarylethene structure, it is preferable that the heteroaryl rings (the heterocycles comprising -Y- or -Z-, shown in structures [i]-[iv]) and R^2 or R^5 form a same plane. For this purpose, it is preferable that the diarylethene structure represented by the general formula [I] has a relatively low-volumed group at the ortho-position of Ar (ortho-position relative to the position at which Ar is bonded to heteroaryl ring)

[0017] Specific examples of Ar include the following formulae:

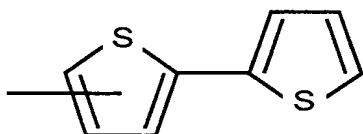
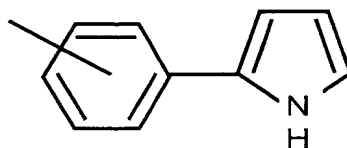
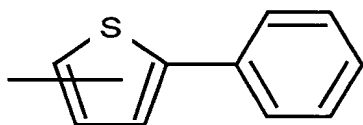
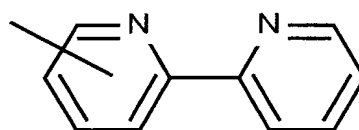
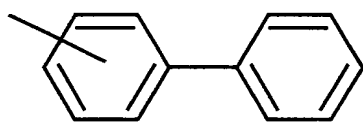
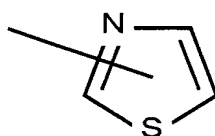
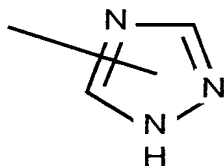
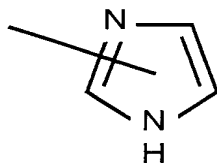
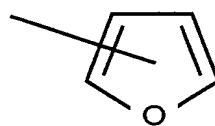
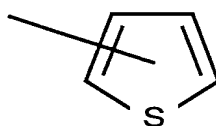
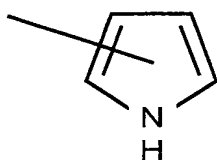
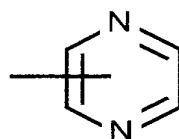
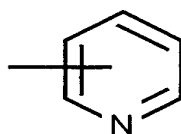
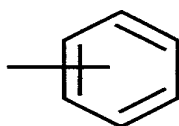
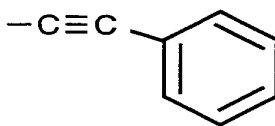
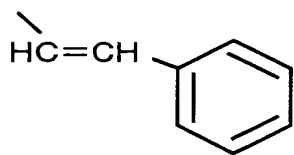




[0018] Preferable specific examples of R^2 and R^5 include the following formulae:

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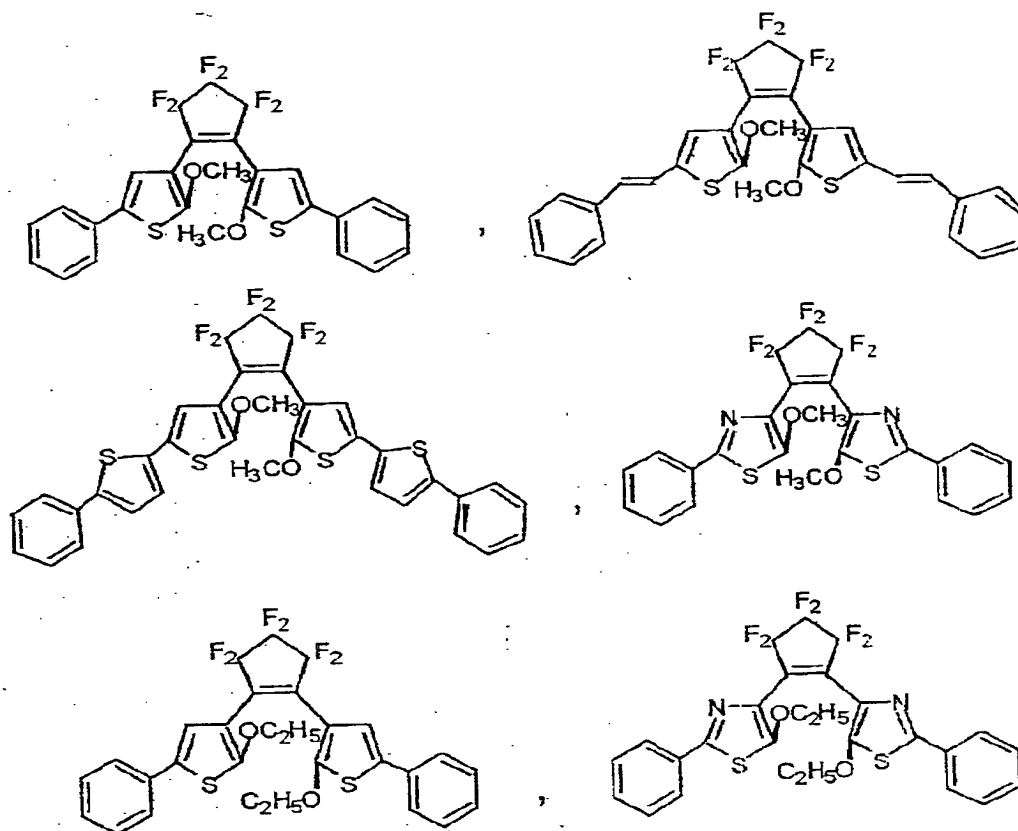
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[0019] In accordance with the present invention, the ring opening quantum yield can be substantially decreased by introducing the above described Ar groups at R² and R⁵, together with alkoxy groups introduced at R¹ and R⁴.

[0020] R³ and R⁶ each represent independently, for example, a hydrogen atom; a linear or branched alkyl group with 1-10 carbon atoms such as methyl group, ethyl group, butyl group, and hexyl group; a linear or branched alkoxy group with 1-10 carbon atoms such as methoxy group, ethoxy group, butoxy group, and hexyloxy group; a halogen atom such as fluorine atom and chlorine atom; a linear or branched fluoroalkyl group with 1-6 carbon atoms such as trifluoromethyl group, pentafluoroethyl group, 2-fluoroethyl group, 2,2-difluoroethyl group, perfluoro-n-hexyl group, and 2-(perfluorobutyl) ethyl group; a cyano group; and an aryl group such as phenyl group and tosyl group which are optionally substituted. A relatively low-volumed group is preferable for R³ and R⁶, a linear alkyl group being especially preferable.

[0021] The examples of compounds belonging to the diheteroarylethene class in accordance with the present invention include the following formulae:



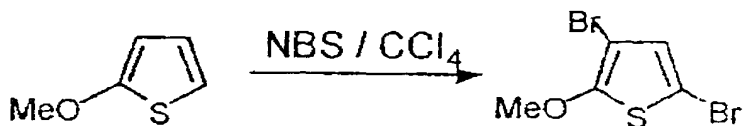
[0022] Each of the above compounds gives rise to ring closing reaction under irradiation of ultraviolet light, efficiently developing color which does not disappear in several hours in room environment, but can stand stably for a longer period of time.

[0023] Hereinafter, the present invention will be described more specifically by way of Synthesis Examples and Examples. However, the present invention is not limited to the following examples.

[0024] Synthesis Example 1: Synthesis of 1,2-bis[2-methoxy-5-phenyl-3-thienyl]perfluorocyclopenten

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[0025] (1-1) Synthesis of 3,5-dibromo-2-methoxythiophene



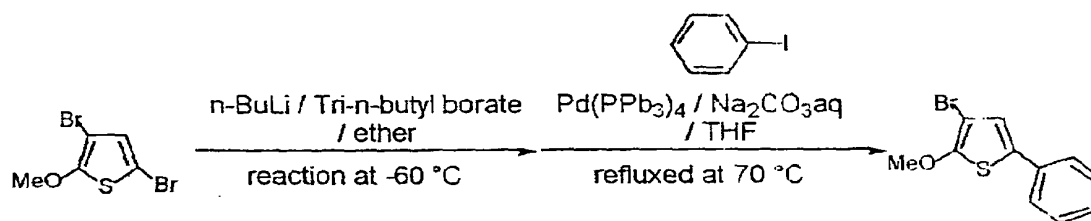
5 **[0026]** 16 g (145 mmol) of 2-methoxythiophene was added into
40 ml of carbon tetrachloride. Then, 51 g (290 mmol) of
N-bromosuccinimide and 250 ml of carbon tetrachloride were
slowly added into it while being stirred in an ice water bath.
After stirred overnight without the water bath, the solution
10 was cooled again in an ice water bath and was filtered by
suction filtration to eliminate solids. The filtrate was
extracted using chloroform, was washed successively with a
sodium bicarbonate aqueous solution and water, and was dried
with addition of magnesium sulfate. The dried extract was
15 condensed after removing magnesium sulfate by filtration. By
developing the product with hexane on a silica gel column,
a colorless liquid was obtained ($R_f = 0.65$). Purification of
the liquid by vacuum distillation (b.p. = 90°C, 8 mmHg) gave
the object compound, 3,5-dibromo-2-methoxythiophene. The
20 yield was 24.6 g in weight and 62.3 % in percentage.

[0027] ^1H NMR (200 MHz, CDCl_3 , TMS): „3.93 (s, 3H), 6.75
(s, 1H),

$\text{MSm/z} = 270, 272, 274$ (M^+)

(1-2) Synthesis of

3-bromo-2-methoxy-5-phenylthiophene



[0028] 250 ml of anhydrous THF was added into 24 g (88 mmol) of 3,5-dibromo-2-methoxythiophene and was cooled to be -78°C with dry ice-methanol. Then, 56 ml (92 mmol) of a solution containing 15 % n-butyllithium hexane was slowly dripped into it. After being stirred for 1 hour, 32 ml (123 mmol) of tri-n-butyl borate was slowly dripped into it and stirred for 2 hours. After being returned to a room temperature, 90 ml of 20 wt% Na_2CO_3 , 18 g (88 mmol) of iodobenzene, and 4.4 g (0.36 mmol) of $\text{Pd}(\text{Ph}_3\text{P})_4$ were added to the solution and refluxed for 5 hours at 70°C . The reaction solution was extracted with ether, washed with a salt solution, and dried with addition of magnesium sulfate. The dried extract was condensed after removing magnesium sulfate by filtration. By developing the product with hexane on a silica gel column, a colorless solid 3-bromo-2-methoxy-5-phenylthiophene was obtained ($R_f = 0.35$). The yield was 15 g in weight and 63 % in percentage.

[0029] ^1H NMR (400 MHz, CDCl_3 , TMS): δ 4.00 (s, 3H), 6.98 (s, 1H), 7.2-7.5 (m, 5H)

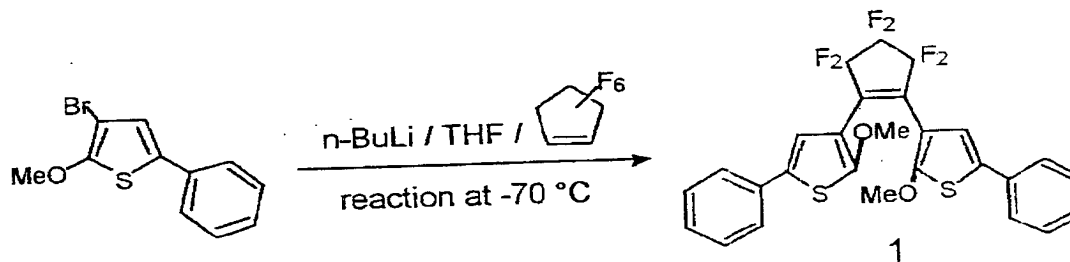
$\text{MSm/z} = 268, 270 (\text{M}^+)$

Anal. Calcd for $\text{C}_{11}\text{H}_9\text{BrOS}$: C=49.09, H=3.37

Found: C=49.20, H=3.38

[0030] (1-3) Synthesis of

1,2-bis[2-methoxy-5-phenyl-3-thienyl]perfluorocyclopentene (compound 1)



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[0031] 140 ml of anhydrous THF was added into 14 g (52 mmol) of 3-bromo-2-methoxy-5-phenylthiophene under argon atmosphere and was cooled to -60°C or lower in dry ice-methanol bath. Then, 36 ml (52 mmol) of a solution containing 15 % n-butyllithium hexane was slowly dripped into it and stirred for 1 hour. Then, 3.5 ml (26 mmol) of perfluorocyclopentene in 10 ml of anhydrous THF was slowly dripped into it at -60°C or lower and was stirred for 2 hours. After being quenched by addition of methanol, the reaction solution was washed with 1N hydrochloric acid and was extracted with ether. The organic phase was washed with water, was dried with magnesium sulfate, and was condensed after magnesium sulfate was removed by filtration. By developing the product with hexane:chloroform = 9:1 solvent on a silica gel column, the compound 1 was isolated ($R_f = 0.56$). The yield was 7.2 g in weight and 50 % in percentage.

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[0032] ^1H NMR (400 MHz, CDCl_3 , TMS): „3.71 (s, 3H), 7.15

(s, 1H), 7.2-7.5 (m, 5H)

MSm/z = 552 (M⁺)

¹H NMR (200 MHz, CDCl₃, TMS): „3.71 (s, 6H), 7.16 (s, 2H),
7.2-7.5 (m, 10H)

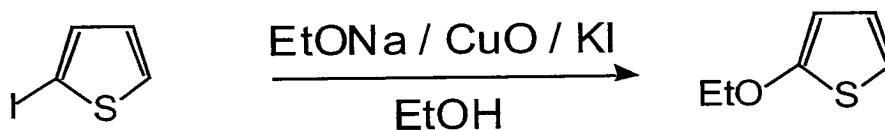
5 Anal. Calcd for C₂₇H₁₈F₆O₂S₂: C=58.69, H=3.28

Found: C=58.87, H=3.37

Synthesis Example 2: Synthesis of

1,2-bis[2-ethoxy-5-phenyl-3-thienyl]perfluorocyclopentene

(2-1) Synthesis of 5-methoxy-2-phenylthiophene



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[0033] 15 g (69 mmol) of 2-iodothiophene, 9.4 g (140 mmol)
of sodium ethoxide, 2.7 g (35 mmol) of copper oxide, and 80
ml of anhydrous ethanol were added into a flask under argon
atmosphere and were refluxed for two nights. Further, 7.0 g

15 (100 mmol) of sodium ethoxide and 57 ml (0.35 mmol) of
potassium iodide were added to it until material spots
disappeared in TLC, and were refluxed for 7 hours. The
reaction solution was returned to a room temperature, was
filtered by suction filtration, and was mixed with ice water.

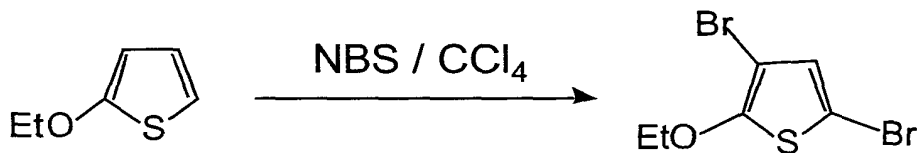
20 The reaction solution was then extracted with ether, was
washed with a salt solution, and was dried with magnesium
sulfate. After filtering out the magnesium sulfate and
evaporating the solvent, the product was subjected to vacuum
distillation (b.p.= 56°C, 8 mmHg) to give a colorless oil of
25 5-methoxy-2-phenylthiazole. The yield was 3.1 g in weight and

57 % in percentage.

MSm/z = 128 (M^+)

^1H NMR (200 MHz, CDCl_3 , TMS): „1.41 (t, $J=7$ Hz, 3H), 4.09 (q, $J=7$ Hz, 2H), 6.20 (d, $J=3.6$ Hz, 1H), 6.53 (d, $J=5.8$ Hz, 1H), 6.71 (t, $J=4.8$ Hz, 1H)

(2-2) Synthesis of 3,5-dibromo-2-ethoxythiophene



[0034] 40 ml of carbon tetrachloride with 8.5 g (48 mmol) of N-bromosuccinimide was slowly added into 8 ml of carbon tetrachloride with 3.1 g (24 mmol) of 2-ethoxythiophene while being stirred in an ice water bath. Then, the ice water bath was removed and stirring was continued overnight. The reaction solution was cooled in an ice water bath and was filtered to remove solids by suction filtration. The reaction solution was then extracted with chloroform, was washed with sodium bicarbonate, sodium thiosulfate, and water, and was dried with magnesium sulfate. After filtering out the magnesium sulfate and evaporating the solvent, the product was developed with hexane on a silica column to give thin yellow oil of 3,5-dibromo-2-ethoxythiophene ($R_f = 0.48$). The yield was 6.5 g in weight and 94 % in percentage.

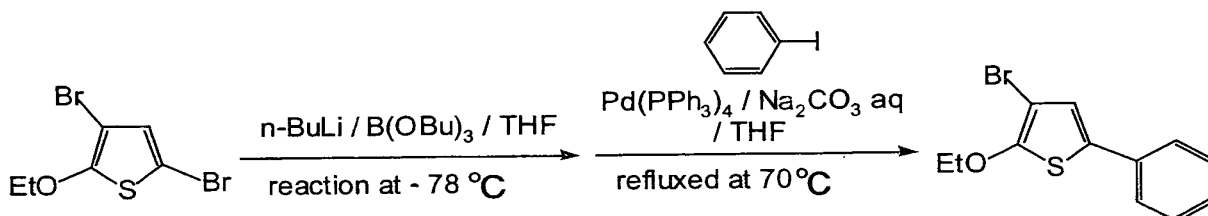
MSm/z = 284, 286, 288 (M^+)

^1H NMR (200 MHz, CDCl_3 , TMS): „1.43 (t, $J=7$ Hz, 3H), 4.13 (q, $J=7$ Hz, 2H), 6.75 (s, 1H),

Anal. Calcd for $C_6H_6Br_2OS$: C=25.20, H=2.11

Found: C=25.50, H=2.14

(2-3) Synthesis of 3-bromo-2-ethoxy-5-phenylthiophene



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[0035] 150 ml of anhydrous THF and 6.5 g (23 mmol) of 3,5-dibromo-2-ethoxythiophene was added into a flask under argon atmosphere. Then, 15 ml (25 mmol) of a solution containing 15 % n-butyllithium hexane was slowly dripped into it at -78°C . After being stirred for 1 hour at -78°C , 9.1 ml (34 mmol) of tri-n-butyl borate was slowly dripped into it and was stirred for 1.5 hours. After being returned to a room temperature and quenched with water, 4.6 g (23 mmol) of iodobenzene, 1.1 g (0.95 mmol) of $\text{Pd}(\text{PPh}_3)_4$, and 50 ml of 20 wt% Na_2CO_3 aqueous solution was added to the solution and was refluxed overnight at 70°C . The reaction solution was extracted with ether, was washed with a salt solution, and was dried with magnesium sulfate. After filtering out the magnesium sulfate and evaporating the solvent, the product was developed with hexane on a silica column to give 3-bromo-2-ethoxy-5-phenylthiophene ($R_f = 0.31$). The yield was 4.9 g in weight and 76 % in percentage.

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$\text{MSm/z} = 282, 284 \text{ (M}^+)$

$^1\text{H NMR}$ (200 MHz, CDCl_3): δ 1.48 (t, $J=7$ Hz, 3H), 4.21 (q,

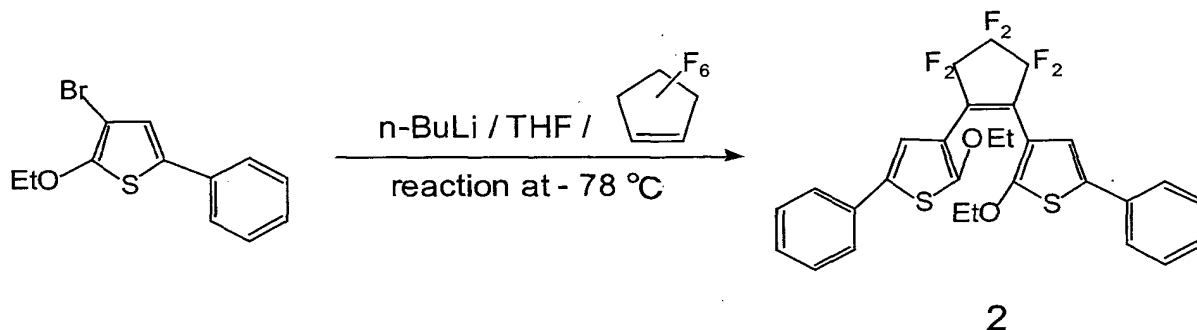
$J=7$ Hz, 2H), 6.98 (s, 1H), 7.25-7.49 (m, 5H),

Anal. Calcd for $C_{12}H_{11}BrOS$: C=50.90, H=3.92

Found: C=51.17, H=3.89

(2-4) Synthesis of

- 5 1,2-bis[2-ethoxy-5-phenyl-3-thienyl]perfluorocyclopentene
(compound 2)



[0036] 4.9 g (17 mmol) of

- 10 3-bromo-2-ethoxy-5-phenylthiophene and 45 ml of anhydrous
THF was added into a flask under argon atmosphere. Then, 12
ml (19 mmol) of a solution containing 15% n-butyllithium hexane
was slowly dripped into it at -78°C . After being stirred for
1.5 hours at -78°C , 5 ml of anhydrous THF with 1.2 ml (34 mmol)
15 of perfluorocyclopentene was slowly dripped into it and was
stirred for 3 hours. After being returned to the room
temperature and being quenched with water, the reaction
solution was washed with 1N hydrochloric acid. The reaction
solution was extracted with ether, was washed with a salt
20 solution, and was dried with magnesium sulfate. After
filtering out the magnesium sulfate, the product was
developed with hexane:chloroform = 7:3 solvent on a silica

gel column to isolate

1,2-bis[2-ethoxy-5-phenyl-3-thienyl]perfluorocyclopentene that is the compound 2. The yield was 1.8 g in weight and 36 % in percentage.

5 MSm/z = 580 (M^+)

^1H NMR (200 MHz, CDCl_3): δ 1.08 (t, $J=7$ Hz, 6H), 3.92 (q, $J=7$ Hz, 4H), 7.22 (s, 2H), 7.26-7.51 (m, 10H),

Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{F}_6\text{O}_2\text{S}_2$: C=59.99, H=3.82

Found: C=60.03, H=3.80

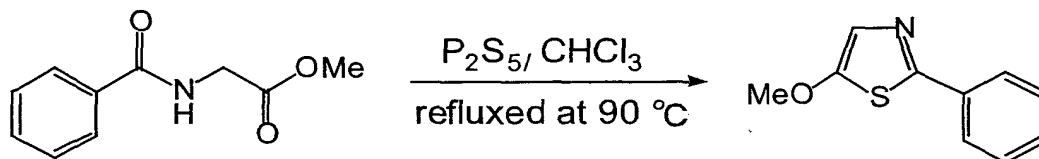
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Synthesis Example 3: Synthesis of

1,2-bis[5-methoxy-2-phenyl-3-thiazoyl]perfluorocyclopentene

(3-1) Synthesis of 5-methoxy-2-phenylthiazole

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[0037] 1.0 g (5.2 mmol) of benzoylglycine methyl ester and 1.4 g (6.4 mmol) of diphosphorous pentasulfide was added quickly into a reaction vessel. After that, anhydrous chloroform (15 ml) was also added and heated to around 80°C . When decrease in hydrogen sulfide generation and white precipitate formation in the reaction solution were observed, an argon balloon was attached and the solution was refluxed for 24 hours. After completion of reaction, the precipitate was dissolved by adding an aqueous solution of strong alkali

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to the solution, and the organic phase was extracted with dichloromethane, followed by drying with addition of magnesium sulfate and removal of solvent. The product was developed with ethyl acetate:hexane = 5:5 solvent on a silica column to give 5-methoxy-2-phenylthiazole ($R_f = 0.40$). The yield was 566 mg in weight and 57 % in percentage.

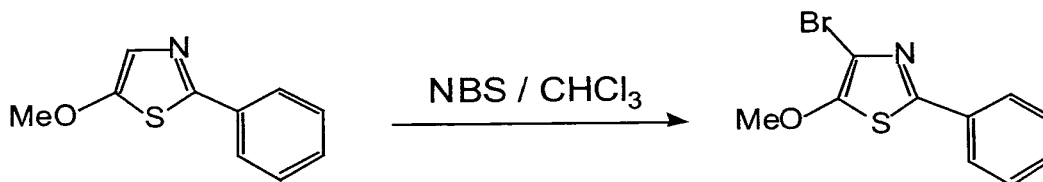
MSm/z = 191 (M^+)

1H NMR (200 MHz, $CDCl_3$): δ 7.84-7.80 (m, 2H), 7.60-7.40 (m, 3H), 6.65 (br s, 1H), 4.27 (d, $J=4.8$ Hz, 2H), 3.82 (s, 3H),

Anal. Calcd for $C_{10}H_9NOS$: C=62.80, H=4.74, N=7.32

Found: C=62.64, H=4.78, N=7.34

(3-2) Synthesis of 4-bromo-5-methoxy-2-phenylthiazole



[0038] 400 mg (2.1 mmol) of N-bromosuccinimide was added into 10 ml of anhydrous chloroform with 400 mg (2.1 mmol) of 5-methoxy-2-phenylthiazole under $0^\circ C$ condition and was stirred for 4 hours at a room temperature. After completion of reaction, the organic phase was extracted with ethyl acetate, and was dried with addition of magnesium sulfate. After removing the solvent, the product was developed with ethyl acetate:hexane = 1:3 solvent on silica column to give 4-bromo-5-methoxy-2-phenylthiazole ($R_f=0.50$). The yield was 550 mg in weight and 97 % in percentage.

MSm/z = 271 (M^+)

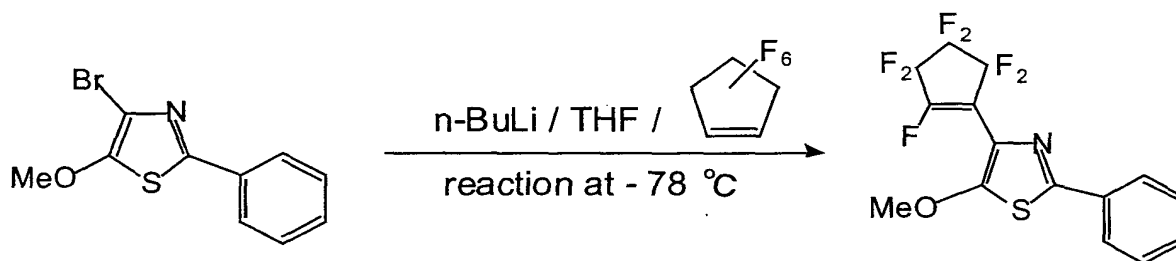
^1H NMR (200 MHz, CDCl_3 , TMS): δ 7.85–7.78 (m, 2H),
7.45–7.36 (m, 3H), 4.03 (s, 3H),

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{NOSBr}$: C=44.46, H=2.98, N=5.18

Found: C=44.56, H=2.99, N=5.19

5 (3-3) Synthesis of

1-[5-methoxy-2-phenyl-3-thiazolyl]perfluorocyclopentene



[0039] 8 ml of anhydrous THF was added into 540 mg (2.0
10 mmol) of 4-bromo-5-methoxy-2-phenylthiazole under argon
atmosphere and was cooled to -78°C or lower with a methanol
solution of dry ice. 1.3 ml (2.1 mmol) of a solution containing
15% n -butyllithium hexane was dripped slowly into it and was
stirred for 15 minutes. Then, 0.2 ml (0.93 mmol) of
15 perfluorocyclopentene was added in 2 ml of anhydrous THF, was
slowly dripped into it at -78°C or lower, and was stirred for
2.5 hours. After being quenched by addition of water, the
reaction solution was extracted with ether. The organic phase
was washed with water and was dried with magnesium sulfate,
20 was filtered to remove the magnesium sulfate, and was
concentrated. The product was developed with hexane:ethyl
acetate = 1:3 solvent on a silica gel column to isolate
1-[5-methoxy-2-phenyl-3-thiazolyl]perfluorocyclopentene (R_f

= 0.30). The yield was 510 mg in weight and 72 % in percentage.

MS m/z = 383 (M^+)

^1H NMR (200 MHz, CDCl_3 , TMS): „7.88-7.80 (m, 2H),
7.48-7.40 (m, 3H), 4.13 (s, 3H),

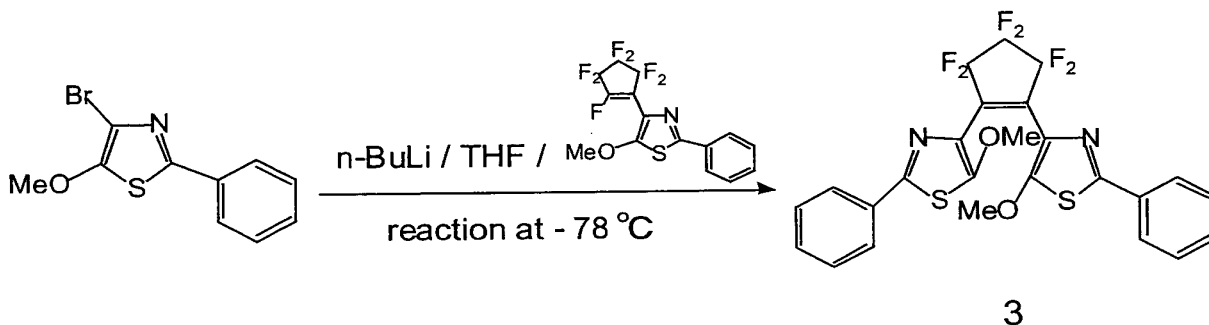
5 Anal. Calcd for $\text{C}_{15}\text{H}_8\text{NOSF}_7$: C=47.00, H=2.10, N=3.65

Found: C=47.25, H=2.08, N=3.66

(3-4) Synthesis of

1,2-bis[5-methoxy-2-phenyl-3-thiazoyl]perfluorocyclopentene
ne (compound 3)

10



[0040] 8 ml of anhydrous THF was added into 540 mg (2.0 mmol) of 4-bromo-5-methoxy-2-phenylthiazole under argon atmosphere and was cooled to -78°C or lower with a methanol solution of dry ice. 1.3 ml (2.1 mmol) of a solution containing
15 15% n -butyllithium hexane was dripped slowly into it and was stirring for 15 minutes. Then, 510 mg (1.33 mmol) of 1-[5-methoxy-2-phenyl-3-thiazoyl]perfluorocyclopentene was added into 2 ml of anhydrous THF, was slowly dripped into it at -78°C or lower, and was stirred for 2.5 hours. After
20 quenching by addition of water, the solution was extracted with ether. The organic phase was washed with water, was dried with magnesium sulfate, was filtered to remove the magnesium

sulfate, and was concentrated. The product was developed with hexane:ethyl acetate = 3:7 solvent on a silica gel column to isolate

1,2-bis[5-methoxy-2-phenyl-3-thiazolyl]perfluorocyclopentene that is the compound 3 ($R_f = 0.10$). The yield was 540 mg in weight and 68 % in percentage.

MS $m/z = 554$ (M^+)

1H NMR (200 MHz, $CDCl_3$, TMS): δ 7.86-7.74 (m, 4H), 7.44-7.35 (m, 6H), 3.83 (s, 6H),

Anal. Calcd for $C_{25}H_{16}N_2O_2S_2F_6$: C=54.15, H=2.91, N=5.05
Found: C=54.25, H=2.97, N=5.10

Example 1

[0041] The compound 1 synthesized in Synthesis Example 1 was dissolved in hexane. This solution was irradiated with light of 313 nm. The solution developed blue color of which absorption maximum was observed at 625 nm ($\epsilon = 1.5 \times 10^4 M^{-1} cm^{-1}$). The generation quantum yield of the colored substance (in the closed-ring form) was determined to be 0.44. The blue color showed no remarkable fading even when irradiated with visible light. The ring opening quantum yield corresponding to fading was determined to be 1.7×10^{-5} .

(Measuring procedure for ring closing quantum yield)

[0042] (1) Hexane solutions in the open-ring forms of the compound 1 and of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (the compound 2) as a comparative sample were prepared. The

both solutions were adjusted to make their absorbance at irradiation wavelength of 309 nm (absorption maximum wavelength of the compound 1 in the open-ring form) to be the same level within a range from 0.2 to 0.3.

5 **[0043]** (2) The solution volumes in absorption cells were equalized.

[0044] (3) In measurement, the absorbance changes of the closed form compounds at absorption maximum wavelength in visible light region (the compound 1: 625 nm, the compound
10 2: 575 nm) were detected. The compound 1 and the compound 2 as a comparative sample were irradiated with light of 309 nm using a xenon lamp, and measurements were made for 10 points in absorbance range of detected wavelength of about 0-0.1.

[0045] (4) The absorbance changes relative to time were
15 plotted, and, from comparison of inclinations for the both compounds, a ring closing quantum yield of 0.44 was obtained for the compound 1 (the quantum yield of the compound 2 was 0.59).

[0046] A quantitative measurement of fading tendency was
20 conducted as follows. The fading by light was hardly observed.

(Measuring procedure for ring opening quantum yield)

[0047] (1) A hexane solution of the compound 1 was prepared and was irradiated with ultraviolet light (wavelength 313 nm)
25 to adjust its absorbance at a wavelength of 625 nm, which is the absorption maximum wavelength in visible light region, to be about 0.5. The hexane solution was irradiated with a light of 625 nm using a xenon lamp and was measured for every

time period for which the absorbance may be changed by about 0.01.

[0048] (2) Fulgide was used as a comparative sample. A toluene solution of the fulgide was prepared and was irradiated with light of 492 nm. The absorbance at a wavelength 492 nm was measured at several points in the approximate changing range of from 0.5 to 0.2, similarly to the case of the compound 1.

[0049] (3) Using an actinometer, the light quantities at wavelengths of 692 nm and of 492 nm were measured.

[0050] (4) Values of $\log(10^A - 1)$ (wherein A represents absorbance) were plotted against time. From the inclination of the plotting which was corrected using the values of light quantities obtained in (3), the relative quantum yield was determined. As a result, the quantum yield of fading reaction (ring opening reaction) was determined to be 1.7×10^{-5} . Even when the solution was exposed to ambient light for three months, no fading (ring opening reaction) was observed.

Example 2

[0051] The compound 1 (10 mg) synthesized in Synthesis Example 1 and 200 mg of polystyrene were dissolved in 3 mL of toluene, and the solution was cast on a Teflon plate to form a polystyrene film having a thickness of 500 μ m.

Irradiation of light of 366 nm onto the film instantly colored the film in blue color. This blue color showed no fading (ring opening reaction) even when exposed to ambient light for three months.

Example 3

[0052] The compound 2 synthesized in Synthesis Example 2 was dissolved in toluene, and the solution was irradiated with
5 light of 313 nm. The solution developed blue color of which absorption maximum was observed at 625 nm ($\epsilon = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The generation quantum yield of the colored substance (in the closed form) was determined to be 0.48. The blue color showed no remarkable fading even when irradiated with visible
10 light. The ring opening quantum yield corresponding to fading was determined to be 2.5×10^{-4} .

(Measuring procedure for ring closing quantum yield)

[0053] (1) Hexane solutions in the open-ring forms of the
15 compound 2 and of fulgide as a comparative sample were prepared. The both solutions were adjusted to make their absorbance at irradiation wavelength of 310 nm (absorption maximum wavelength of the compound 3 in the open-ring form) to be the same level within a range from 0.2 to 0.3.

20 [0054] (2) The solution volumes in absorption cells were equalized.

[0055] (3) In measurement, the absorbance changes of closed form compounds at absorption maximum wavelength in visible light region (the compound 2: 625 nm, the fulgide:
25 492 nm) were detected. The compound 2 and the fulgide were both irradiated with light of 310 nm using a xenon lamp, and measurements were made for 10 points in absorbance range of detected wavelength of from about 0 to about 0.1.

[0056] (4) The absorbance changes relative to time were plotted and, from comparison of inclinations for both compounds, a ring closing quantum yield of 0.48 was obtained for the compound 2 (the quantum yield of fulgide was 0.20).

5 [0057] A quantitative measurement of fading tendency was conducted as follows. The fading by light was hardly observed.

(Measuring procedure for ring opening quantum yield)

[0058] (1) A hexane solution of the compound 2 was prepared
10 and was irradiated with ultraviolet light (wavelength 313 nm) to adjust its absorbance at a wavelength of 625 nm, which is the absorption maximum wavelength in visible light region, to be about 0.4. The hexane solution was irradiated with a light of 625 nm using a xenon lamp and was measured for every
15 time period for which the absorbance may be changed by about 0.01.

[0059] (2) Fulgide was used as a comparative sample. A toluene solution of the fulgide was prepared and was irradiated with light of 492 nm. The absorbance at a
20 wavelength 492 nm was measured at several points in the approximate changing range of from 0.4 to 0.2, similarly to the case of the compound 2.

[0060] (3) Using an actinometer, the light quantities at wavelengths of 625 nm and of 492 nm were measured.

25 [0061] (4) Values of $\log (10^A - 1)$ (wherein A represents absorbance) were plotted against time. From the inclination of the plotting which was corrected using the values of light quantities obtained in (3), the relative quantum yield was

determined. As a result, the quantum yield of fading reaction (ring opening reaction) was determined to be 2.5×10^{-4} .

Example 4

5 **[0062]** The compound 3 synthesized in Synthesis Example 3 was dissolved in toluene, and the solution was irradiated with light of 313 nm. The solution developed violet color of which absorption maximum was observed at 555 nm ($\epsilon = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The generation quantum yield of the colored substance
10 (in the closed-ring form) was determined to be 0.29. The violet color showed no remarkable fading even when irradiated with visible light. The ring opening quantum yield corresponding to fading was determined to be 3.3×10^{-4} .

15 (Measuring procedure for ring closing quantum yield)

[0063] (1) Toluene solutions in the open-ring forms of the compound 3 and of fulgide as a comparative sample were prepared. The absorbance of the both solutions at irradiation wavelength of 313 nm were adjusted to a same level within a
20 range from 0.2 to 0.3.

[0064] (2) The solution volumes in absorption cells were equalized.

[0065] (3) In measurement, the absorbance changes of closed form compounds at absorption maximum wavelength in
25 visible light region (compound 3: 555 nm, fulgide: 492 nm) were detected. The compound 3 and the fulgide were both irradiated with light of 313 nm using a xenon lamp, and measurements were made for 10 points in absorbance range of

detected wavelength of from about 0 to about 0.1.

[0066] (4) The absorbance changes relative to time were plotted and, from comparison of inclinations for both compounds, a ring closing quantum yield of 0.29 was obtained
5 for the compound 3 (the quantum yield of fulgide was 0.20).

[0067] A quantitative measurement of fading tendency was conducted as follows. The fading by light was hardly observed.

(Measuring procedure for ring opening quantum yield)

10 [0068] (1) A toluene solution of the compound 3 was prepared and was irradiated with ultraviolet light (wavelength 313 nm) to adjust its absorbance at a wavelength of 555 nm, which is the absorption maximum wavelength in visible light region, to be about 0.4. The hexane solution
15 was irradiated with a light of 555 nm using a xenon lamp and was measured for every time period for which the absorbance may be changed by about 0.01.

[0069] (2) Fulgide was used as a comparative sample. A toluene solution of the fulgide was prepared and was
20 irradiated with light of 492 nm. The absorbance at a wavelength 492 nm was measured at several points in the approximate changing range of from 0.4 to 0.2, similarly to the case of the compound 3.

[0070] (3) Using an actinometer, the light quantities at
25 wavelengths of 555 nm and of 492 nm were measured.

[0071] (4) Values of $\log(10^A - 1)$ (wherein A represents absorbance) were plotted against time. From the inclination of the plotting which was corrected using the values of light

quantities obtained in (3), the relative quantum yield was determined. As a result, the quantum yield of fading reaction (ring opening reaction) was determined to be 3.3×10^{-4} .

5 INDUSTRIAL APPLICABILITY

[0072] As described in detail hereinabove, according to the present invention, a photochromic material is provided which has a substantially low ring opening quantum yield, practically no fading problem under ambient light, and an
10 excellent long-time stability of recorded or displayed information.

[0073] The photochromic material of the present invention has possible applications not only for the production of optical memory media and optical display materials, but also
15 to novel optical elements.